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Spectrophotometric Determination of Molybdate (MoO_4^{2-}) Using Tannic acid as a Reagent.

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ABSTRACT

Simple, sensitive and accurate spectrophotometric method was proposed for the micro determination of molybdate(MoO_4^{2-}) using Tannic acid as a reagent. The method was based on the formation of 1:2 orange colored complex between the anion and TA. The optimum conditions for the determination were established. The Beer's law was applicable in the range of 0.2-5.0 µg/cm^3. The method detection limit, limit of quantification, molar absorptivity, Sandell's sensitivity, coefficient of correlation (β) were reported. The method is free from common interferences. The method was successfully applied for the determination of Mo (VI) in environmental water samples and pharmaceutical products.

Keywords: Spectrophotometric determination, molybdate, Tannic acid, environmental water samples, pharmaceutical products.

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INTRODUCTION

Molybdenum is the 54th most abundant element in the Earth's crust and the 25th most abundant element in the oceans. Though molybdenum is found in minerals such as wulfenite, ferrimolybdite, powellite, the main commercial source of molybdenum is molybdenite (MoS_2). These ores typically occur in conjunction with ores of tin and tungsten. Molybdenum is mined as a principal ore, and is also recovered as a byproduct of copper and tungsten mining[1].Molybdenum does not occur naturally as a free metal on earth, but rather in various oxidation states. The free element is a silvery metal with a grey cast. In its compounds it shows different oxidation states like -2, 0, +1 to +6, the most common and stable being +4 and +6.

Molybdate is an essential trace element for plants and animals and a vital factor in nutrition for several metalloenzymes to function correctly. At least 50 molybdate-containing enzymes were known by 2002, mostly in bacteria, and their number is increasing with every year[2,3]. Those enzymes include aldehyde oxidase, sulfite oxidase and xanthine oxidase[4]. Because of its involvement in the processes of N_2 fixation, nitrate reduction and the transport of nitrogen compounds in plants, molybdate plays a crucial role in nitrogen metabolism of plants[5]. Molybdate is a component of vitamin and mineral supplements. Molybdate in the form of magnesium molybdate is used in the treatment of anaemia[6]. A study of molybdate compounds as potential anti-diabetic agents is reported. Oxo anions ($[MO_4]^{2/3-}$, where M = V, Cr, Mo or W) have anti-diabetic properties[7]. Combination of molybdate with the medicinal plant *Teucrium polium L*. can improve islet cells function before their transplantation. It results in greater insulin secretion[8].

In addition it is widely used in a variety of industrial processes being an important constituent of metal alloys, pigments, lubricants among others. It’s ability to withstand extreme temperatures without significantly expanding or softening makes it useful in applications that involve intense heat, including the manufacture of armor, aircraft parts, electrical contacts, industrial motors and filaments.

High levels of molybdate can interfere with the body's uptake of copper, producing copper deficiency in ruminants. Molybdate prevents plasma proteins from binding to copper, and also increases the amount of copper that is excreted in urine. Ruminants that consume high amounts of molybdates develop symptoms including diarrhoea, stunted growth, anaemia and achromotrichia (loss of hair pigment). These symptoms can be alleviated by the administration of more copper into the system, both in dietary form and by injection[9].Because molybdate toxicity is associated with copper intake or depleted copper stores in the body, humans who have an inadequate intake of dietary copper or some dysfunction in their copper metabolism that makes them copper-deficient could be at greater risk of molybdate toxicity. But a more detailed research is needed on molybdate toxicity in humans.

Sparingly soluble compounds (e.g. molybdenum disulphide, metal, dioxide) are less toxic than those that are more easily soluble (e.g.trioxide, ammonium molybdate). Increased blood uric acid concentrations and gout-like symptoms have been reported among workers exposed to molybdates in a copper–molybdenum plant[10].

When inhaled, both metallic molybdenum and sparingly soluble molybdenum trioxide have been reported to damage the lungs. Possible reasons for the low degree of molybdenum toxicity are the facts that molybdate is a necessary trace element in the body and is rapidly excreted through urine[11,12].

A variety of methods have been reported for the determination of anions[13-15] while many methods have been developed for determination of molybdates which include atomic emission spectrometry with inductively coupled plasma[16], neutron activation analysis[17], spectrofluorimetry[18], flow injection technique[19], electrochemical technique[20] and graphite furnace atomic absorption spectrometry[21].

Various Gravimetric[22] and Volumetric[23] methods are known for the determination of molybdenum as molybdate but they are time consuming and not accurate.

Spectrophotometry is the most common technique used for the determination of molybdates because of its high sensitivity and selectivity. Many spectrophotometric methods for the determination of molybdate based on its reaction with thiocyanate in the presence of a reducing agent[24] and with toluene-3,4-dithiol[25] are not favourable as they are not selective and are prone to interferences from other elements.

Spectrophotometric determination of molybdate has been reported using phenylfluorone[26],hydrogen peroxide[27],hydrogen sulphide[28], phenylhydrazine hydrochloride[29], thiocynate using thioglycollic acid as reductant[30], xylenol orange[31], thiolactic acid[32], chloranilic acid[33].

Although several methods have been reported for the spectrophotometric determination of Molybdates, they suffer from drawbacks such as lack of reproducibility, stability, interferences and requirements of prior extraction and heating.

The aim of this work is to develop a simple, fast, cost effective, and interference-free method for the determination of MoO_4^{2-} that would be useful in a routine water quality laboratory or pharmaceutical laboratory.

MATERIALS AND METHODS

Apparatus

All glass wares used for experimental purpose were made up of Pyrex or corning glass. The burette, pipette and standard flasks were calibrated by the method described by Vogel[34].

Instruments

pH meter: A digital pH meter was used for pH measurements. The pH meter was calibrated by employing the buffer solutions of pH 4.0, 7.0 and 9.2. Spectrophotometer: The absorption measurements were carried out on a Bausch and Lomb spectronic -20, using 1cm matched glass cell. The spectrophotometer was calibrated by measuring the absorption spectra of potassium chromate in KOH solution and that of potassium permanganate in sulphuric acid solution[35].

Preparation of experimental solution

The stock solution of molybdate(1000 ppm) was prepared by dissolving 1.932g of ammonium molybdate in 250 cm^3 of distilled water and standardized gravimetrically[36].Tannic acid solution was prepared by dissolving weighed amount in distilled water and then diluting up to the mark.

Preparation of foreign ion solutions

The solutions of cations and anions were prepared by dissolving their A.R. grade salts in distilled water or dilute acids as required. The solutions of various anions were prepared by dissolving their A.R. grade sodium, potassium or ammonium salts in distilled water.

Procedure for spectrophotometric determination of molybdates using tannic acid as a reagent

To 1 cm^3 of an aqueous solution containing varying amounts of 50 µg of MoO_4^{2-},1 cm^3 of 1% tannic acid was added. The pH of the solution was between 6.5-7.5, the final volume was made upto 10 cm^3 with distilled water. The amount of molybdate was determined from a calibration curve prepared by processing solutions containing known amounts of molybdate through recommended procedure and plotting the absorbance against the concentration of MoO_4^{2-}.

Absorption spectra

To determine absorption spectra, 0.3127×10^{-3}M MoO_4^{2-}solution was used.

Effect of reagent concentration

The effect of reagent concentration was studied by varying the reagent concentration from 0.05% to 2% and keeping all the parameters constant. From the value of absorbance, the minimum concentration of reagent required for the analysis of molybdate was determined.

Stability of the complex

The stability of the color of the complex was determined by measuring the absorbance of the complex at different time intervals at 435 nm.

Calibration curve

A series of solutions containing varying amounts of MoO_4^{2-}were treated as per procedure developed for spectrophotometric determination of MoO_4^{2-}.The calibration curve was prepared by plotting absorbance versus concentration of MoO_4^{2-} in ppm. The calibration curve obtained was employed for determination of MoO_4^{2-}in unknown samples.

Precision and accuracy

Precision and accuracy of the method developed were determined by carrying out 10 replicate analysis of solutions each containing 5.0 µg of MoO_4^{2-}. The average of 10 replicate determinations was taken to calculate standard deviation, variance, and variation from mean at 95% confidence limit.

Procedure for job's continuous variation method

$0.3127x10^{-3}$M MoO_4^{2-}solution was prepared. 1cm^3 of same molar tannic acid was mixed. Series of solutions containing 0.25-4.0 cm^3 of $MoO_4^{2-}$and 4.75-1.0 cm^{3}of reagent were taken. The total volume of each mixture was made up to 10 cm^3 with distilled water. These mixtures were treated as per the procedure described for spectrophotometric determination of $MoO_4^{2-}$and their absorbance was recorded at 435 nm. The absorbance was plotted against the mole fraction.

Procedure for mole ratio method

A series of solutions were prepared by mixing 1 cm^3 of $0.3127x10^{-3}$MMoO_4^{2-} and 0.5-5.0 cm^3 of same molar reagent. Each mixture was treated according to the procedure developed and the absorbance of these solutions was measured against reagent blank at 435 nm. Absorbance obtained was plotted against the mole ratio of the concentration of reagent to MoO_4^{2-}.

Interference study

The effect of diverse ions on determination of 5.0 µg MoO_4^{2-} was studied by mixing a definite amount of the desired foreign ions with the MoO_4^{2-}solutions and then treated as per the developed procedure. The tolerance limit was taken as the amount of ion causing an error of not more than ±2% in the absorbance values of MoO_4^{2-}. These results revealed that various cations and anions can be tolerated at satisfactory levels. However Mn^{2+}, Zr^{4+}, Sr^{3+}, Ce^{2+}, Al^{3+}, Zn^{2+}, Pb^{2+}, Fe^{2+}interfered seriously. The interference of some of these ions could be masked by using $C_2O_4^{2-}$(2 ml of 5000 µg cm^{-1}), thiourea (1 ml of 0.5%) and CH_3COO^- (1 ml of 5000 µg cm^{-1}) up to 100 µg cm^{-1}.

Determination of molybdates in synthetic mixtures and real samples

A number of synthetic mixtures of molybdates and other commonly associated anions were prepared and treated as per the developed procedure. Environmental water samples were spiked with known amounts of molybdate (MoO_4^{2-}) and analyzed by the proposed general procedure. Each filtered environmental water sample was analyzed for molybdate. They tested negative. To these samples known amount of molybdate (MoO_4^{2-}) was added and then analyzed by the proposed procedure.

Determination of molybdates in pharmaceutical samples

Each multi mineral tablet was crushed to a fine powder, weighed and treated with 15 cm^3 of conc.HNO_3. The mixture was then evaporated to dryness. The residue was leached with 7 cm^3 of dilute H_2SO_4, boiled and cooled. To this mixture 10 cm^3 of distilled water was added, the solution was boiled again and cooled. The solution was filtered and diluted to 50 cm^3 with distilled water.

Zinc and phosphate interfere seriously. Zinc was removed gravimetrically[37], while phosphate was removed quantitatively by the method described in the literature[38]. The filtrate obtained after removal of zinc and phosphate was diluted upto 100 cm^3. An aliquot of this solution was analyzed by the present method for molybdate determination after adjusting its pH between 6.5-7.5.

Determination of molybdates in environmental water samples

100 cm^3 of each environmental water sample was boiled and reduced to 25 cm^3. It was treated with 1 cm^3 of conc. HNO_3 and heated. The solution was filtered after neutralizing with dilute ammonia and diluted to appropriate amount with distilled water. Each filtered sample was analyzed for molybdate. They tested negative. To these samples known amount of molybdate (MoO_4^{2-}) was added and then analyzed by the proposed procedure.

RESULTS AND DISCUSSION

Absorption spectra

The proposed method involved the formation of an orange color between molybdate and tannic acid in a medium of pH 6.5-7.5. The absorption spectra of solution containing orange colored complex against the reagent blank and that of tannic acid solution against blank is shown in the Figure 1. The figure revealed that the complex has maximum absorbance at 435 nm. The reagent has no appreciable absorbance at specified wavelengths. Hence further studies were carried out at 435 nm. The color reaction was found to be instantaneous.

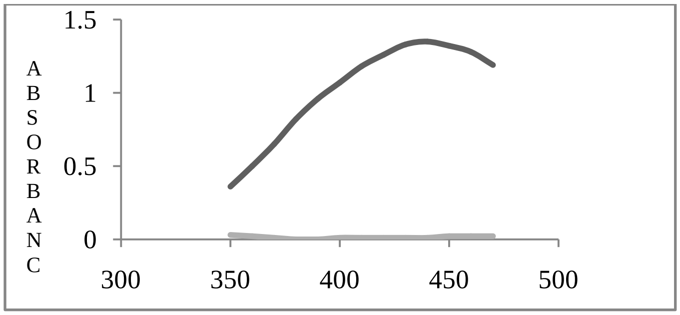

Figure 1: Absorption spectra

(Series 1: Complex against Reagent blank, Series 2: Tannic acid solution against Blank)

Effect of pH

The effect of pH on the intensity of the color reaction is shown in the Figure 2. The absorbance was found to be maximum in the pH range 6.5-7.5. Hence further analytical investigations were carried out in media of pH 7.5.

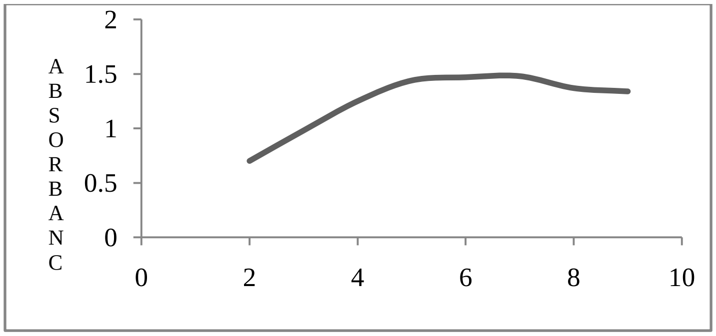

Figure 2: Effect of pH

Effect of reagent tannic acid concentration and stability of the complex

The studies of effect of various concentrations of the reagent on the color reaction reveal that, quantitative analysis is obtained with concentration of 1.0% and above (Figure 3). However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. Hence 1 ml of 1.0% tannic acid solution was employed throughout the experimental work. The complex was found to be stable for three hours.

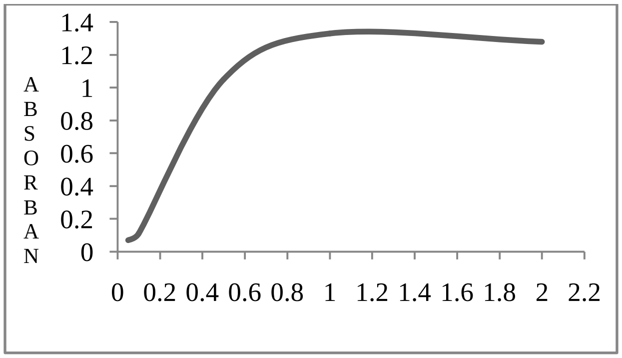

Figure 3: Effect of reagent concentration

Calibration curve

The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of molybdate. A linear calibration graph drawn between absorbance and molybdate concentration indicates that MoO_4^{2-} may be determined in the range 0.02-5.0µg/cm^3. This range was also confirmed from Ringbom's plot. The calibration graph is shown in the Figure 4.

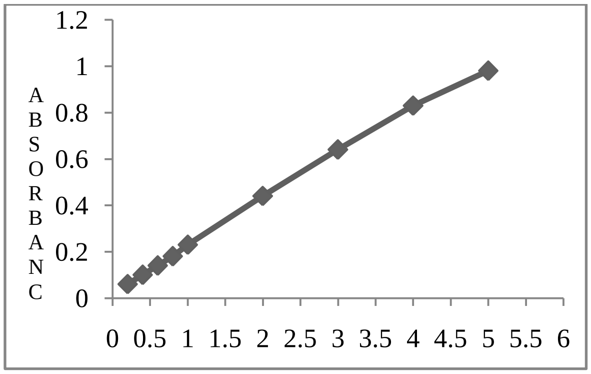

Figure 4: Calibration curve

Stoichiometry of the molybdate-tannic acid complex

The stoichiometry of the complex was determined by Job's method of continuous variation and by mole ratio method. It was found to be 1:2 (MoO_4^{2-}:Ligand). The plots are shown in Figure 5 and 6 respectively.

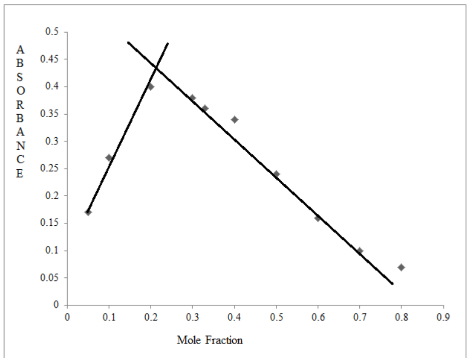

Figure 5: Job's continuous variation method

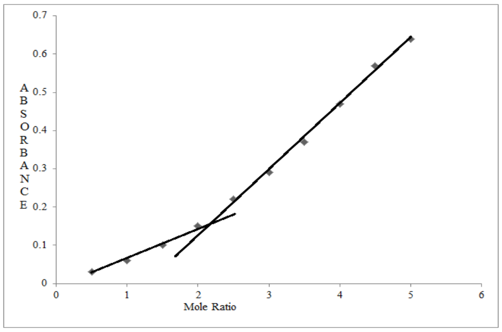

Figure 6: Mole Ratio method

Precision and accuracy

The precision and accuracy of the developed method for the determination of molybdate was tested by analyzing the solutions containing 5.0 µgof MoO_4^{2-}. The average of 10 replicate analyses was 4.94 which vary between 4.94±0.028 at 95% confidence limit. The standard deviation was 0.0394and the variance was 0.0016.

In conclusion the analytical parameters pertaining to the proposed method are given in Table 1 while the values obtained for precision and accuracy are given in Table 2.

Table 1: Analytical parameters pertaining to the proposed method

Molar absorptivity	0.03707 L mol $^{-1}$ cm $^{-1}$
Sandell's sensitivity	0.02749 µg cm^{-1}
Beer's law range	0.2 –5.0 µg cm^{-1}
Regression coefficient of MoO_4^{2-} on absorbance	4.863
Regression coefficient of MoO_4^{2-} on absorbance	0.2052
Correlation coefficient	0.998

Table 2: Precision and Accuracy

Absorbance(O.D.)	Amount of MoO_4^2 found in µg	$(x - x)^2$
0.98	4.90	0.0016
0.98	4.90	0.0016
0.99	4.95	0.0001
0.99	4.95	0.0001
1.00	5.00	0.0036
0.99	4.95	0.0001
0.98	4.90	0.0016
0.98	4.90	0.0016
1.00	5.00	0.0036

Table 3: Tolerance limit of diverse ions

Anions	Tolerance Limit(µg)	Cations	Tolerance Limit(µg)
NO_3^-, NO_2^-, CH_3COO, SO_3^{2-}, Br^-, Cl^-, SO_4^{2-}, SCN^-, BrO_3^-, $C_2O_4^-$	5000	Cu^{3+}, Ni^{2+}	1000
WO_4^{2-}	2000	Ca^{2+}, Hg^{2+}, Th^{4+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Sn^{2+}, $^{a}Fe^{2}$	100
EDTA, IO_3^-, Borax, $S_2O_3^{2-}$	1000	$^{b}Ce^{2+}$, $^{b}Sr^{3+}$, Al^{3+}, $^{c}Zn^{2}$	below 100
Citrate, Tartarate, $^{d}S_2O_8^{2-}$	100		
IO_3^-	below 100		
NO_3^-, NO_2^-, CH_3COO^-, SO_3^{2-}, Br^-, Cl^-, SO_4^{2-}, SCN^-, BrO_3^-, $C_2O_4^-$	5000	Cu^{3+}, Ni^{2+}	1000
WO_4^{2-}	2000	Ca^{2+}, Hg^{2+}, Th^{4+}, $Mg^{2,}$ Ba^{2+}, Cd^{2+}, Sn^{2+}, $^{a}Fe^{2}$	100
EDTA, IO_3^-, Borax,	1000	$^{b}Ce^{2+}$, $^{b}Sr^{3+}$, Al^{3+}, $^{c}Zn^{2+}$, Pb^{2+}, $^{b}Zr^{4+}$, $^{b}Mn^{2+}$, Fe^{3+}	below 100
$^{e}PO_4^{3-}$	100		

a- Masked by 1 ml 0.5% thiourea, b-Masked by 2 ml of $C_2O_4^{2-}$ (5000 µg)

c- Removed gravimetrically, d- Masked by 1 ml of CH_3COO^- (5000 µg)

e. Removed quantitatively by magnesium nitrate reagent

Effect of diverse ions

The effect of interfering ions on the proposed method was investigated. The tolerance limit was considered to be the amount that caused a ±2% deviation in the absorbance value. The results are summarized in Table 3. These results reveal that various cations and anions can be tolerated at satisfactory levels.

Analytical applications

The proposed method under the already established optimum conditions was applied for the determination of MoO_4^{2-} in synthetic samples, environmental water samples and pharmaceutical products. The results presented in Table 4 and 5indicate the successful applicability of the proposed method to real sample analysis.

Table 4: Determination of Mo(VI) in Synthetic Mixtures

Synthetic mixtures	MoO_4^2 Added(µg)	[a]Amount found(µg cm^{-1})	%Recovery
MoO_4^{2-}(2µg)+CH_3COO^-(4µg)	**2**	2.13±0.058	106.50
MoO_4^{2-}(4µg)+WO_4^{2-}(8µg)	**4**	4.07±0.058	101.80
MoO_4^{2-}(5µg)+IO_3^-(6µg)+$S_2O_8^-$(10µg)	**5**	4.83±0.058	96.60

a- Mean± standard deviation (n=3)

Table 5: Determination of Mo (VI) in Environmental water samples and Pharmaceutical samples

Sample	MoO_4^{2-} Added(µg)	Proposed Method		[31]Reference method	
		[a]Found ± SD	%Recovery	[a]Found± SD	%Recovery
[b]Water samples					
i)Thane	0.4	0.43±0.029	107.50	0.38±0.073	95.00
ii)Rabale	0.8	0.82±0.029	102.50	0.77±0.029	96.25
Pharmaceutical Samples	Labelled claim(µg)				
[c]i)Maxum	25	25.20±0.15	100.80	-	-
[d]ii)Zincovit	25	24.60±0.11	98.40	-	-

Mean± Standard deviation (n=3)

a- Gave no test for molybdate.

b- Maxum®- Eris Lifesciences Pvt. Ltd., Gujarat. (each tablet contains Calcium D Pantothenate 10 mg, Zinc sulphate 15 mg, Cupric oxide 1.5 mg, Manganese chloride 2 mg, Chromium chloride 65 mcg, Calcium dibasic phosphate 162 mg, Ferrous sulphate 33.3 mg, Biotin 30 mcg, Magnesium oxide 50 mg, Sodium molybdate 25mcg).

c- Zincovit®- apex laboratories private limited. (each tablet contains Zinc 22 mg, Magnesium 18 mg, Manganese 0.9 mg, Copper 0.5 mg, Iodine 150 mcg, Boron 150 mcg, Selenium 50 mcg, Chromium 25 mcg, Molybdenum 25 mcg, Silica 1 mg).

CONCLUSION

The proposed method for the determination of molybdate ion is simple, rapid, sensitive and has the advantage of enabling a wide range of determination without the need for extraction or heating. When compared to other techniques which require pre-concentration process and separation prior to analysis, the present method is not time consuming and gives accurate results. The satisfactory applicability of the proposed procedure to the determination of molybdates in various samples shows the utility of the method. Although many sophisticated and high cost instrumental techniques like ICP-MS, AAS, etc. are available for the determination of molybdates at trace levels, the factors such as the low cost of the instrument, ease of handling, lack of need for consumables, and almost no maintenance have caused spectrophotometry to remain a popular and inevitable technique, particularly in the laboratories of developing countries with a limited budget.

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